EFFECT OF INCREASING FREE SPACE ABOVE THE CHARGE ON THE COMPOSITION
AND YIELD OF THE VOLATILE PRODUCTS FROM COAL CARBONIZATION

C. Ortuglio, J. G. Walters, and D. E. Wolfson

U. S. Department of the Interior, Bureau of Mines
Pittsburgh Coal Research Center, Pittsburgh, Pa. 15213

ABSTRACT

The effect of increasing the free space above the charge on the composition and yields of the volatile products from the carbonization of Pittsburgh-bed coal and one industrially used blend from the eastern United States and one from western United States was investigated with the BM-AGA carbonization apparatus.

Increasing the free space above the charge from 1 inch to 3 inches, to 6 inches and to 9 inches resulted in lower tar yields and increased gas and light oil yields. Anthracene and naphthalene yields were increased, quinoline and benzene insoluble fractions of both the tar and pitch increased considerably with increased free space, although the carbon content of the tars and pitches increased only slightly.

Increased cracking, a result of the increase in free space, caused a decrease in the yields of tar acids, tar bases, neutral oils, olefins, aromatics, and paraffins and naphthenes. Gas composition was relatively constant; hydrogen and methane tended to increase and ethane decrease.

Results of the investigation are being used to design a unit to upgrade the volatile products of carbonization by cracking the hot products as they leave the carbonization chamber.

INTRODUCTION

The Bureau of Mines, in cooperation with the American Gas Association, jointly developed a pilot-scale carbonization test apparatus (BM-AGA) to determine the carbonization characteristics of coals and to evaluate the byproduct yields (5).

Although the BM-AGA test apparatus is used primarily to determine the coking characteristics of coals for metallurgical use, the objective of this investigation was to determine the effect of cracking on the quality of carbonization products by varying the free space above the coal charge when the temperature is kept constant.

Carbonization yields are influenced by the rank of coal carbonized, whereas their composition is primarily a function of the temperature and contact time of the evolved vapors with the heated surfaces within the retort or ovens. Decomposition of vapors proceeds in two steps: Primary decomposition of gaseous vapors as they are evolved from the plastic layer at moderate temperatures and then pass through the hot coke surfaces, and secondary decomposition as the vapors pass through the free space above the coal charge with less contact surface. Porter (4) in a study of coal carbonizing equipment has found that the variance of contact time of the gases and vapors passing through the heated spaces in approved industrial ovens may be 100 percent or more.

EXPERIMENTAL PROCEDURES

Procedure and apparatus for BM-AGA carbonization tests have been described in detail in a previous publication (5). Basically, the apparatus consists of a cylindrical steel retort, electrically controlled resistance-type furnace, product

recovery train, gas scrubbers, meters, and sampler. The standard retort used through-
out this investigation is 26 inches high and 18 inches in diameter. The results from
previous carbonization tests, using standard retorts and 900°C carbonization tempera-
tures have been correlated with industrial (7) and experimental oven (6, 8) data. The
coal charges were adjusted in height so as to leave 1-, 3-, 6-, and 9-inches of free
space above the coal charge. Duplicate carbonization tests were made at 900°C and the
results reported are averages of two determinations.

A single coal (1166) and two commercial coal blends (1161 and 1167A) were used in
this investigation. Coal 1161 was carbonized as received so that the size consist
would be comparable to that charged at the coke plant. Coals for tests 1166 and 1167A
were received separately in lump form and were crushed in the hammer-mill and blended.

In computing yields from BM-AGA carbonization tests, the quantitative yields are
based on U. S. gallons (231 cubic inches) and short tons (2,000 pounds). Coke yields
are reported as dry coke, weight-percent of coal carbonized. The yield, specific
gravity (determined), and gross heating value of the gas are reported as stripped of
light oil and saturated with water vapor at 60°F and under a pressure equivalent to
30 inches of mercury. Light oil refers to the crude product stripped from the gas.
Liquor includes the fixed ammonia and absorbed free ammonia. Ammonium sulfate is re-
ported in pounds per ton of coal and includes the total free and fixed ammonia. The
tar yield, properties, and constituents are reported on a dry basis and includes only
that light oil which condenses with the tar, and the specific gravity of the tar is
reported at 15.5°C/15.5°C.

The yields of carbonization products are given on the as-carbonized basis (table
1). The latter basis is used to compare coals when the moisture and ash contents
differ significantly. Comparisons lose their significance because a high percentage
of ash or moisture makes the yield of coke or liquor artifically high and those of
other products correspondingly low. The calculation of moisture- and ash-free basis
assumes that all ash remains in the coke and that all moisture in the coal is recov-
ered as liquor.

Properties of Tar

The tar yields are affected by coal rank, temperature of carbonization and free
space above the coal charge. The temperature of carbonization is the most signifi-
cant contributing factor in determining tar quality. Increased free space permits
the vapors to remain longer at the higher temperature resulting in considerable vari-
ations in tar quality.

The effect of free space on tar quality is presented in table 2. Cracking of tar
due to increased free space resulted in progressive increases in its specific gravity,
naphthalene yield, anthracene yield, except for the 9-inch free space and a reduction
in tar acids, bases, and neutral oils. It is interesting to note that unlike naphtha-
lene, the anthracene yield was slightly less at the 9-inch free space for all tests.
There was no significant change in the residue yield.

The chemical composition of tars and pitches is presented in table 3. As ex-
pected, the carbon content increased and the hydrogen content decreased with progres-
sive increases in the free space.

Quinoline (1) and benzene (free carbon) (5) insoluble values for the tars and
pitches, as well as the softening point of the pitches were determined. These are
critical factors, commercially important, in determining the suitability of coal tar
pitches as electrode binders. The tar values were determined on the whole tar and
the pitch values were determined on the +350°C fraction of the tar. The cube-in-air
method was used to determine the softening point of the pitches. The results are
presented in table 4.

Table 1. - Yields of carbonization products, as-carbonized basis

Coal number	Free space inches	Yields, weight-percent							Yields per ton of coal			
		Coke	Gas	Tar	Light oil	Liquor	Free ammonia	Total	Gas cu. ft.	Tar gallons	Light oil in gas gallons	Ammonium sulfate, pounds
1161	1	65.9	18.2	5.8	1.13	8.8	0.160	100.0	10,450	11.9	2.81	21.3
	3	65.6	16.5	5.5	1.17	10.2	.177	99.1	10,640	11.2	3.25	23.6
	6	65.7	16.2	5.5	1.23	10.3	.180	99.1	10,770	11.1	3.42	22.8
	9	65.5	16.3	5.3	1.13	10.0	.209	98.4	10,790	10.2	3.16	23.1
1166	1	66.3	14.9	7.6	1.28	8.8	.166	99.0	10,400	15.8	3.57	25.3
	3	66.3	15.3	8.1	1.24	8.0	.168	99.1	10,750	16.5	3.45	23.7
	6	66.4	15.3	7.7	1.31	7.6	.173	98.5	10,700	15.2	3.64	22.6
	9	66.4	15.2	7.5	1.37	7.7	.174	98.3	10,850	14.8	3.81	22.1
1167A	1	70.8	13.6	6.7	1.16	7.0	.163	99.4	10,140	13.7	3.23	23.2
	3	70.7	13.9	6.4	1.15	6.2	.161	98.5	10,290	12.9	3.20	20.8
	6	70.7	13.9	6.2	1.24	6.1	.164	98.3	10,350	12.1	3.47	20.0
	9	70.7	14.1	6.1	1.21	6.3	.149	98.6	10,490	11.9	3.36	18.8

Table 2. - Specific gravity and component tar yields

Coal number	Void space inches	Specific gravity of tar	Yields, gallons per ton				Neutral Oils			Yields, pounds per ton	
			Acids	Bases	Neutral oils	Residue	Olefins	Aromatics	Paraffins and Naphthenes	Naphthalene	Anthracene
1161	1	1.17	0.52	0.33	3.50	6.82	0.39	2.95	0.16	5.36	2.81
	3	1.19	.35	.27	2.89	6.60	.31	2.52	.06	7.42	3.58
	6	1.20	.20	.22	2.31	7.10	.25	2.04	.02	8.70	5.25
	9	1.23	.11	.15	1.63	7.03	.17	1.45	<.01	9.55	4.71
1166	1	1.16	.78	.32	3.95	10.26	.33	3.52	.10	3.57	1.36
	3	1.18	.55	.28	3.69	10.87	.32	3.33	.04	7.20	2.34
	6	1.20	.25	.24	2.57	10.89	.29	2.26	.02	10.32	3.27
	9	1.21	.20	.22	2.20	10.86	.24	1.95	.01	11.59	2.52
1167A	1	1.17	.69	.27	3.50	8.68	.31	3.14	.09	4.14	1.92
	3	1.19	.37	.26	2.41	8.82	.20	2.19	.03	7.53	3.12
	6	1.22	.21	.18	1.98	8.54	.21	1.76	.01	8.97	3.31
	9	1.22	.17	.17	1.78	8.57	.21	1.57	.01	9.92	2.95

Table 3. - Effect of free space on the chemical composition of tar and pitch

Void space, inches	Tar				Pitch			
	1	3	6	9	1	3	6	9
Coal 1161								
Hydrogen..........	5.7	5.2	5.0	4.7	4.8	4.4	4.3	3.9
Carbon.............	90.5	91.4	92.7	93.1	92.3	92.8	93.8	94.2
Nitrogen..........	1.1	1.2	1.1	1.0	1.4	1.3	1.2	1.0
Oxygen.............	2.2	1.7	0.7	0.7	1.1	1.1	0.3	0.4
Sulfur.............	0.4	0.4	.4	.4	0.3	0.3	.3	.3
Ash................	.1	.1	.1	.1	.1	.1	.1	.2
Coal 1166								
Hydrogen..........	5.4	5.0	4.8	4.7	4.9	4.7	4.6	4.2
Carbon.............	89.7	90.4	90.8	91.1	90.5	91.0	91.9	92.1
Nitrogen..........	1.3	1.3	1.2	1.1	1.5	1.4	1.3	1.3
Oxygen.............	2.5	2.2	2.1	2.0	2.1	2.0	1.3	1.6
Sulfur.............	1.0	1.0	1.0	1.0	0.8	0.7	0.7	0.7
Ash................	0.1	0.1	0.1	0.1	.2	.2	.2	.1
Coal 1167A								
Hydrogen..........	5.8	5.4	5.1	5.0	4.9	4.7	4.6	4.4
Carbon.............	90.3	92.0	91.5	92.0	91.1	91.6	92.0	92.2
Nitrogen..........	1.3	1.3	1.3	1.3	1.5	1.4	1.4	1.3
Oxygen.............	1.4	0.4	1.0	0.6	1.7	1.5	1.2	1.3
Sulfur.............	1.0	.8	1.0	1.0	0.7	0.7	0.7	0.7
Ash................	0.2	.1	0.1	0.1	.1	.1	.1	.1

Table 4. - Effect of free space above coal charge on quinoline and benzene insolubles

Coal number	Void space, inches	Tar[1]		Pitch[1]		Softening point, °C
		Quinoline insolubles	Benzene insolubles	Quinoline insolubles	Benzene insolubles	
1161	1	1.70	6.61	3.85	25.95	119.0
	3	2.73	8.17	3.96	24.25	105.0
	6	4.84	11.29	8.87	28.33	110.0
	9	11.07	17.42	22.03	32.55	138.0
1166	1	2.26	8.64	2.82	22.55	96.8
	3	4.13	11.60	4.78	26.55	101.0
	6	7.29	14.26	9.14	28.33	94.0
	9	11.15	18.76	14.34	30.87	85.8
1167A	1	2.57	7.66	2.86	21.75	94.0
	3	3.87	10.34	4.73	23.70	94.3
	6	6.39	12.47	7.60	25.15	82.3
	9	9.50	15.46	12.15	27.85	85.0

[1] Weight-percent for tar and pitch.

The insolubility values for all tars and pitches increased with increasing free space. There were marked increases at the 9-inch free space for all tests, indicating the formation of insoluble high boiling hydrocarbons.

Properties of Gas

Properties of byproduct gas vary with carbonizing conditions as well as with coal characteristics. An investigation (9) of the gas yielded by coals carbonized by the BM-AGA method at 900°C showed that the physical and chemical properties of the gas depend on the rank of coal.

The yield of carbonization gas increases with increased carbonization temperature; similarly, maintaining the effluent vapors at elevated temperatures by increasing the free space above the coal charge exposes the vapors to high temperatures for a longer time resulting in degradation of the volatile material with a still greater increase in the gas yield. Davis and Auvil (3) have attributed this increase to greater cracking of hydrocarbons in the enlarged free space. Table 1, confirms these results, in that the gas yield increases with increased free space.

The chemical and physical properties of the gas are presented in table 5. Two important properties of gas are its heating value and hydrogen sulfide content. The heating value, generally considered to be the most important property of byproduct gas, is presented on both the cubic foot and pound-of-coal basis. The greatest heat recovery for the longest exposure time of gas in the retort was 112 Btu per pound of coal (1167A) or a gain of 224,000 Btu per ton of coal. Coal 1161 showed a steady decline in heating value with increased exposure time.

The hydrogen sulfide content of the gas, calculated to grains per 100 cubic feet of gas, is becoming increasingly important because of air pollution restrictions, and must be reduced to limited concentrations before disposal. Results indicate that the formation of hydrogen sulfide is related to exposure time; however, the concentration of hydrogen sulfide in the byproduct gas is dependent on the sulfur content of the coal and is not related to coal rank. Although the sulfur content for coal 1167A (1.4 percent) was higher than that for coal 1161 (0.6 percent), the net increase in hydrogen sulfide, attributed to free-space cracking, was only 14.8 percent, compared with 26.0 percent for coal 1161.

Light Oil

The composition of light oil, like the tar, is a function of the carbonizing conditions of which temperature, free space above the coal charge, and the contact time of the gas in the hot free space are the most important; however, the total yield of light oil under normal carbonizing conditions is dependent largely upon the rank of the coal.

Benzene, the principal constituent of the light oil, is a decomposition product whose formation is accelerated under conditions favorable to cracking effluent vapors.

The percent composition of benzene in the light oil, as presented in table 6, progressively increased with an increase in free space, whereas all other constituents of light oil were adversely affected by the free space increases.

The total light oil yield reached a maximum at the 6-inch free space for the coal blends and at the 9-inch free space for the straight coal.

Table 5. - Chemical and physical properties of gas

Coal number	Void space, inches	Composition, dry, volume-percent					Heating value		Hydrogen sulfide grains per 100 cu.ft.
		hydro-gen	Carbon monoxide	Methane	Ethane	Ethylene	Btu per cu.ft.	Btu per lb.coal	
1161	1	60.87	5.98	25.78	2.43	5.03	618	3,235	131
	3	62.13	6.07	24.51	2.15	5.14	608	3,231	157
	6	64.01	5.07	23.79	1.60	5.53	600	3,180	157
	9	63.29	5.91	27.40	1.08	2.32	576	3,121	165
1166	1	59.38	6.49	30.08	1.42	2.63	603	3,133	638
	3	59.37	6.13	30.11	1.56	2.83	608	3,268	714
	6	59.09	6.45	30.97	0.92	2.57	601	3,221	707
	9	61.87	4.52	29.85	.75	2.96	596	3,189	828
1167A	1	63.91	4.31	28.81	1.30	1.67	583	2,956	561
	3	61.94	5.12	30.05	0.85	2.04	587	3,020	600
	6	61.98	5.15	30.08	.70	1.29	581	3,007	606
	9	61.91	4.85	30.94	.56	1.74	585	3,068	644

Table 6. - Composition of light oil, gallons per ton

Coal number	Void space, inches	Benzene	Toluene	m,p-xylene	o-xylene	Ethyl-benzene
1161	1	2.24	0.38	0.12	0.05	0.01
	3	2.65	.42	.14	.04	.006
	6	2.91	.40	.09	.01	.004
	9	2.89	.22	.04	.01	-
1166	1	2.77	.64	.13	.02	.004
	3	2.79	.55	.08	.02	.003
	6	3.13	.45	.05	.01	.001
	9	3.34	.42	.04	.01	.001
1167A	1	3.05	.06	.10	.02	.013
	3	3.05	.05	.07	.02	.003
	6	3.39	.04	.03	.01	.001
	9	3.30	.03	.03	.01	.001

Properties of Coke

The physical properties of the cokes were determined by standard methods of the American Society for Testing Materials (2). The tumbler indices, 1-inch stability and 1/4-inch hardness, are the only coke properties reported as these parameters are most commonly used in evaluating metallurgical coke.

Variations of free space had no effect on the coke yield. The only significant change in the coking properties was for coal 1166 in which the 1-inch stability index was progressively lowered from 33 for the 1-inch free space to 28 for the 9-inch free space. The stability and hardness indices for both coal blends remained essentially the same.

CONCLUSIONS

The yields of carbonization products are influenced by the rank of coal used and the temperature of carbonization. The primary decomposition is influenced by the rate of heating and the secondary decomposition by the time of contact of the vapors while in the hot retort and is dependent on the volume of free space per unit volume of charge.

The cracking of tar due to increased free space resulted in progressive increases in specific gravity, naphthalene yield, anthracene yield (except for the 9-inch free space test) and a reduction in tar acids, bases, and neutral oils.

Free space increases had no effect on the coke yield or coke properties except for the 1-inch tumbler stability for coal (1166) which was progressively lowered with increased free space.

The light oil yield was increased and reached a maximum at the 6-inch free space for the coal blends, and the 9-inch free space for the straight coal.

There was a progressive increase in gas yield, with the greatest variation of 500 cubic feet per ton of coal and the heat recovery for the longest exposure of gas in the retort was 112 Btu per pound of coal.

Increased free space above the coal charge during carbonization, permitted longer residence time of the vapors at a specific temperature and improved the quality of the byproducts. However, since coke is the major and most valuable product of coal carbonization, it would be economically infeasible to decrease the capacity of commercial ovens. In recognition of this, the Bureau of Mines is investigating the upgrading of volatile materials, in a separate cracking unit, outside of the coking furnace. Results of this investigation will be published in a subsequent report.

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